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20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)*

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Spectrochemical Measurements with Multichannel Integrating Detectors

by

R.B. Bilhorn, P.M. Epperson, J.V. Sweedler and M.B. Denton

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Department of Chemistry
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ABSTRACT

This is the second article in a two part series describing the operation, performance characteristics, and spectroscopic application of Charge Transfer Devices (CTDs) in analytical chemistry. The first article in the series describes the new generation of integrating multi-channel detectors, the charge injection device (CID) and the charge-coupled device (CCD). The first article also discusses the spectroscopically pertinent characteristics of these detectors and presents performance data for representative devices. This article covers three major topics related to the optimum use of integrating detectors in analytical spectroscopy. The advantages of employing integrating multichannel detectors in analytical spectroscopy rather than a single detector in a wavelength scanning system or an inter-ferometer are discussed. Included are detector read noise considerations which have not been considered in previous performance comparisons. When employing an integrating detector in luminescence,

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INDEX HEADINGS: Charge Transfer Devices, Charge-Coupled Device, Charge Injection Device, Multichannel Emission Spectroscopy, Multichannel Luminescence Spectroscopy, Multichannel Absorption Spectroscopy

Introduction

Recent technological advancement has made available to the analytical chemist new types of multichannel ultraviolet and visible light detectors which offer significant improvements in performance over the time honored photomultiplier tube (PMT). Some of these new multichannel detectors offer improved sensitivity and dynamic range performance. Two classes of these detectors which are currently available are photodiode arrays (PDAs)[1] and charge transfer devices (CTDs).

PDAs have received wide attention in the chemical literature because of their availability for the last ten years. These devices however, do not match the performance of PMTs on a detector element by detector element basis and are of interest in spectroscopy only because of the multichannel advantage that they offer. PDAs have also been successfully applied in a number of one-dimensional imaging applications. CTDs have received comparably less attention in the chemical literature due to their more limited availability in camera systems capable of operating them in the fashion necessary for achieving their full spectroscopic capabilities. These devices do however match, and can often exceed, the capabilities of PMTs on a detector element by detector element basis as discussed in the first article in this series.[2] CTDs are represented by charge-coupled devices (CCDs) and charge injection devices (CIDs), the difference being in the method of charge information read out.

The common feature of CTDs and PDAs is that they store photogenerated charge as light strikes the detector. This is in contrast to the PMT which produces a current as light strikes the photocathode. This integrating nature of CTD's and PDA's strongly influences their optimum application in spectrochemical systems.

The primary noise source in properly operated CTDs and PDAs differs from that in PMTs and photoconductive detectors such as those commonly used in the infrared spectral region. Therefore, to achieve optimum signal-to-noise ratio (SNR) performance with these detectors, different compromises should be made between analysis time and photon integration time. This manuscript provides an overview of the impact of the difference in noise sources between the two types of detectors. Theoretical SNR advantages of spectrometers designed to use multichannel detectors, as compared to spectrometers using single detectors, are presented. Additionally, the results of minimum detectable analyte signal calculations are presented for systems employing integrating detectors. These calculations consider the photon flux conditions commonly encountered near the detection limit in luminescence, absorption and emission spectroscopy. The great sensitivity and flexibility of CTD-based detector systems are illustrated through the discussion of several applications in measurement sciences. The examples provide an overview of the areas in which CTDs are currently being employed, and indicate the kind of performance which is obtainable with these state-of-the-art systems.

SNR of Multichannel & Multiplexed Techniques vs. Single Channel Methods

Currently, there are three popular approaches to measuring light intensity over more than one wavelength interval. The first of these is a sequential technique in which a single detector is employed with a dispersive optical system to monitor the various wavelength intervals individually. Multichannel systems also employ dispersive optics, however more than one detector is used to simultaneously monitor multiple wavelength intervals. The third popular technique involves single channel detection of

multiplexed signals. Michelson interferometry and Hadamard spectroscopy are examples. In these techniques spectral information from multiple wavelength intervals is measured simultaneously but the data is encoded in such a way that intensity information from a single wavelength interval can be extracted.

Until now, the technological limitations associated with detectors have resulted in no one of these instrumental approaches being superior under all conditions. The experimenter has had to carefully choose the instrumental configuration that would offer the best performance under the given set of measurement conditions. It is conceivable however, that as detector technology advances, the tradeoffs between the different optical configurations will become less severe, and at least over a particular wavelength range, a single technique may emerge as superior under most or all conditions.

A comparison of the SNR performance of the various optical configurations for acquiring spectral information from many wavelength intervals is instructive for pointing out some of the advantages and disadvantages of each method. Such a comparison points out the experimental conditions under which certain techniques provide superior SNR performance and the reasons for the advantage.

Comparisons of the SNR merits of various optical configurations for multiwavelength measurements appearing in the literature[3-6] have concluded that multichannel detection should lead to comparable or improved SNR performance as compared to single channel sequential and multiplexed systems given the same total measurement time. These comparisons assume the detectors are equivalent on a detector element by detector element basis and that the same amount of light is available in each method. This previous work

considered current producing detectors such as PMTs and photoconductors and is extended here to include consideration of systems employing integrating detectors.

The relative SNR superiority of multichannel systems over other approaches can be shown to depend on a number of factors including the type of noise source which dominates the intensity measurements and the number of different wavelength intervals (N) which are to be measured. The noise sources tend to be statistically independent, thus their effects add in quadrature. This makes it possible to consider the effects of each type of noise source independently and to evaluate the performance of multiplexed and multichannel systems as compared to single channel systems when one type of noise source dominates.

Noise sources can be categorized as sources that are independent of signal intensity (detector noise), sources which are proportional to signal intensity (source fluctuation noise) and sources that are proportional to the square root of signal intensity (photon shot noise). Photon shot noise arises from the randomness in photon arrival rate at a detector. This results in an uncertainty when measurements of that rate are made in a finite length of time. The photon arrival rate approximates a Poisson distribution so the expectation value for the standard deviation can be shown to be equal to the square root of the signal level.

Detectors such as PMTs and photoconductors, like the popular mercury-cadmium-telluride (MCT) IR detector, have dark current. As shown in the appendix of the first manuscript in this series, the shot noise associated with this dark current ($N_{d,pmt}$) is the limiting detector noise and depends on the square root of the measurement time. Integrating detectors can be cooled to reduce dark current to insignificant levels so this noise

source becomes unimportant in these detectors.[7] A noise introduced when the charge information in a detector element is read out (called the read noise) is the dominant form of detector noise in CTDs and PDAs. This noise source is independent of measurement time.

Table I shows the relative SNR improvements over a single detector sequential system obtainable with a multichannel or multiplexed system under the limiting conditions of noise types listed above. Multichannel and single channel systems employing both PMT type and CTD type detectors are considered. The SNR equations used to arrive at the results shown in Table I are given in appendix 1.

In the case where detector noise dominates, multiplexed detection results in the often cited Fellgett's advantage of $N^{1/2}$. Multichannel detection with a PMT or a photoconductor also results in an advantage of $N^{1/2}$. Detector noise dominance is common with the photoconductive detectors used in the IR resulting in one of the several reasons for the success of FTIR. Multichannel detection with a integrating detector as compared to single channel detection with the same type of detector in a detector noise limited situation results in an advantage of N. This result is due to the time independent read noise. The advantage that a multichannel integrating detector system has over a single channel PMT or photoconductor system depends on the individual detector noise parameters as discussed in the first manuscript and is given by,

$$\frac{SNR_{MC,ctd}}{SNR_{SC,pmt}} = \frac{(tR_dN)^{1/2}}{N_r} \qquad (1)$$

where the definition of the terms are as in Table I and appendix 1.

In photon shot noise limited systems, the nature of the spectrum affects the relative improvement over single channel sequential detection that is possible with multiplexed detection.[8] When broad-band spectra are considered, i.e., signal strength is relatively constant throughout the spectral range, the predicted performance is comparable to that achievable with single channel sequential detection. When narrow or line spectra are considered however, the relative intensity of the line of interest ($f(\nu)$) as compared to the mean intensity of the whole spectrum ($\bar{f}$) determines the magnitude of the advantage (or disadvantage).[8,9] The distributive Fellgett's advantage is

$$G_{snr} = (f(\nu))/\bar{f}E)^{1/2} \qquad (2)$$

where E is the modulation efficiency of the system. Experimenters have observed that the proximity of spectral features of interest to other intense ones determines the observed SNR.[10] Weak spectral features adjacent to intense spectral features are adversely affected, yielding poorer SNR than is obtainable with a single channel system.

Multichannel detection systems are unaffected by the nature of the spectrum when photon shot noise limited conditions prevail. Regardless of whether broad-band or narrow line spectra are being detected, multidetector systems yield a signal-to-noise ratio improvement of $N^{1/2}$, where N is the number of channels, over single detector sequential systems.

Fluctuation noise adversely affects multiplexed systems as compared to single channel sequential systems.[11] Random changes in source intensity in a Michelson interferometer for example, are indistinguishable from changes in detected intensity which are caused by

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changes in interference resulting from mirror movement. As is the case with photon shot noise, the nature of the effect in a multiplexed system depends on the structure of the spectrum being measured. When intensity is relatively constant over the wavelength range, and fluctuation occurs to the same extent at all wavelengths, a multiplex disadvantage of $1/(N)^{1/2}$ is observed.[8,9] If the fluctuation occurs mainly in the intensity of bright spectral lines superimposed on a relatively dark background, the noise tends to be localized in the vicinity of the bright spectral line.

Table I shows that multichannel systems have no advantage over single channel systems when fluctuation noise is dominant. In this case, increasing the measurement time per channel has no affect on measurement SNR because noise accumulates at the same rate as signal (see appendix 1). Fluctuation in some analytical sources however has been observed to follow a 1/f type of behavior over limited ranges.[12] That is, the noise power decreases at higher frequencies. In analytical systems where this is the case, the effects of fluctuation noise can be reduced by decreasing the total measurement time. A multidetector system offers an advantage in this case because the point in time at which fluctuation noise exceeds photon shot noise is reached in all channels approximately simultaneously at 1/N times the time required by a single detector sequential system. Parameters which are changing or drifting do not have the opportunity to change as drastically because the measurement time is reduced. Additionally, since all channels are measured simultaneously, all measurements are made under the same set of

(changing) conditions. If background corrections are to be applied to a particular spectral feature for example, measuring the background at the same time that the measurements of the spectral feature are made can result in more accurate corrections.

The foregoing clearly illustrates the SNR benefits that multi-channel detection offers over single channel sequential detection. It also points out the conditions under which multiplexed detection systems perform poorly. A number of factors other than SNR must be considered when evaluating the overall performance and utility of a particular analytical technique. For example, the absolute wavelength accuracy afforded by interferometric methods of recording spectra is a definite advantage. Nonetheless, SNR is an important figure of merit, especially when highly precise results are desired, or when decreased analysis time allows increased sample throughput rates and improved productivity.

The technological limitations currently facing UV-visible spectroscopy are different from those in IR spectroscopy. In the IR, shot noise and fluctuation noise are seldom observable over detector noise. Conversely, in the UV-visible region of the spectrum, detector noise is seldom the limiting noise source. Thus, single channel multi-plexed methods have much less to offer for UV-visible spectroscopy. Silicon CTDs and PDAs respond with the greatest sensitivity to radiation in the UV-visible region of the spectrum. Therefore, the spectroscopic techniques employed in this region of the spectrum stand to benefit greatly from the application of these new detectors.

A variety of advantages associated with solid-state multichannel detection in addition to SNR enhancements have thus far been neglected. A significant advantage is the increase in flexibility of wavelength selection that is offered as compared to multichannel detection with a number of discrete detectors. This was the primary driving force behind a number of attempts to replace multiple PMTs placed behind laboriously positioned slits with multichannel detectors of far inferior performance (vidicons etc.). Modern CTD and PDA detectors offer a number of other advantages including increased reliability as a result of their ruggedness, relative simplicity of operation and low cost per resolution element. As discussed in the first manuscript, many of these detectors actually exceed the performance capabilities of PMTs adding even further to the multichannel advantages.

A considerable difficulty still facing the widespread application of CTD detectors in analytical spectroscopy is the different geometric requirements placed on optical systems designed to use these detectors as compared to systems designed to use PMTs. The total area available per detector element is considerably smaller than that of a typical PMT photocathode. Current optical systems designed to use PMT detectors are therefor not highly compatible with these detectors. Properly designed spectrometers however offer the advantages of smaller size and the lack of moving parts.

Sensitivity of Spectrochemical Measurements made with
Integrating Photodetectors

CTDs and PDAs are charge integrating detectors rather than current producing detectors. Thus, the methodology required to use a CTD or PDA differs somewhat from that used with a PMT. It is often useful to think of a CTD or PDA as an electronic photographic emulsion. The detectors can be employed for optical spectroscopy in a manner analogous to film. Unlike photographic film however, solid-state array detectors offer the convenience of direct electronic readout providing the ability to perform real time experiment optimization and the convenience of computer based data manipulation.

Fluorescence, phosphorescence or emission intensity measurements can be made directly using a single exposure method. Absorption measurements require either two exposures or use of a portion of the detector array for monitoring incident intensity while another part monitors transmitted intensity. The later approach offers the advantage of reducing the stability requirements on the source.

Low Light Level Sensitivity

The sensitivity that is achievable in luminescence spectroscopy, or emission spectroscopy when there is very little background emission, is dictated by the minimum detectable flux. During the maximum allowable observation time, enough photogenerated charge must be produced to result in a measureable signal. A CTD or PDA that is cooled sufficiently has virtually no dark current and is capable of integration periods in excess of 30 minutes. The practical limit is set by cosmic rays and nuclear decay events that obscure the image. In practice, the long term

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drift (low frequency 1/f noise) associated with most analytical sources usually sets a maximum allowable observation time of several minutes.

Aside from photon shot noise, the only significant noise source in a properly operated CTD or PDA is the read noise. This noise is independent of time and signal level. Once sufficient light has struck the detector to generate enough electron-hole pairs to equal twice the rms read noise, then a measurement SNR of 2 is possible. The sensitivity achievable with a CTD can be very high due to the low read noise of these devices (as low as 5 electrons). The sensitivity of PDAs is several orders of magnitude poorer because of their much higher read noise (typically 1200 to 1500 electrons). With a read noise of 10 electrons (a typical value for a modern CCD), 20 photogenerated charge carriers are required for a detectable signal. Devices having 80% quantum efficiency require 25 photons to produce this quantity of charge. In a two minute experiment, this condition is met by a flux of -0.21 photons per second. In contrast, PMTs have finite dark current rates and the shot noise on the dark current is the limiting noise source. Additionally, PMT photocathode materials generally have lower QEs than CTDs necessitating a higher photon flux to produce the same electron generation rate. For example, a select photon counting PMT[13] with a mean dark count rate of 5 counts per second and a QE of 20% would, over a two minute integration period produce 600 counts of dark current. Assuming the dark current obeys Poisson statistics, the noise would be 24.5 counts ($\sqrt{600}$). To achieve a SNR of 2, 49 counts would be required. Given the inferior quantum efficiency of PMT photo cathodes,

this would require 245 photons or about ten times the flux required by the CCD.

In experimental systems where very low photon fluxes are to be measured, high quantum efficiency and low dark current are of great importance. Source stability is also required so that long integration periods can be used. The multichannel advantage offered by CTDs becomes particularly important when measurements are to be made at many wavelengths. Since multiple wavelength regions are observed simultaneously, the long term stability requirement on the source is reduced by the inverse of the number of different channels. When shorter periods of time must be used, detector read noise must also be low so that it does not dominate the signal measurement. If the experiment must be completed in a short period of time, the disparity in levels of performance between CCDs and PMTs observed above is greatly reduced. On the other hand, the dynamic range performance of photon counting PMTs is much poorer than that of a CCD. Table II shows the characteristics important to low light level detection of optimized CCD, CID, PDA and photon counting PMT systems.

Minimum Detectable Absorbance

In the case of absorption spectroscopy, other detector parameters are of importance. The ability of the detector system to determine the difference between two slightly different intense fluxes determines the minimum detectable absorbance (MDA). When a very dilute solution of an absorbing species is placed in the optical path, very

little attenuation of the source intensity results. Integrating photon detectors such as the CTDs are capable of storing a finite amount of photogenerated charge in any particular detector element. Integration of a photon flux for a period of time which results in an attempt to store more charge than a detector element is capable of containing results in a signal which is not proportional to the amount of photogenerated charge created. In an absorption measurement it is advantageous to integrate the photon signal until just prior to detector element saturation. This results in the maximum SNR. The rms noise on the resulting signal is due primarily to photon shot noise and is approximately equal to the square root of the signal. This is because detector read noise is quite low compared to the square root of the device saturation level and assumes flicker noise in the source is negligible. Properly cooled CTDs have such low dark currents that shot noise from this source is also negligible. The resulting signal to noise ratio is given by:

$$S/N = (\eta \phi_p t)^{1/2} \qquad (3)$$

which assumes a photon flux of ϕ_p over a time interval of t seconds, and a detector quantum efficiency of η. The signal to noise ratio of the measured signal is simply the signal to noise ratio of the incident photon beam degraded by the less than unity quantum efficiency of the detector. Higher quantum efficiency detectors result in higher signal to noise ratios per unit time. Put another way, a higher quantum efficiency detector can attain a given signal to noise ratio in a shorter

period of time. This is true up to the point of detector element saturation in an integrating detector or to the point of maximum anode current or count rate in a PMT. By the above arguments, as the amount of charge that a CTD or PDA detector element can contain increases, the product $\phi_p t$ can increase and the measurement SNR can be improved.

Calculations of the minimum detectable absorbance that is measurable using a single exposure of an integrating photodetector estimate the minimum difference between two intense signals that can be detected.[14] As the saturation level of a CTD or PDA increases, the SNR of the measurement of the incident intensity and the transmitted intensity improve. This improves the precision of the transmittance calculation and hence, allows smaller values of absorbance to be measured. As long as fluxes are high and integration times are short, photon shot noise remains the dominant source of noise and source fluctuation noise can be neglected. Source fluctuation noise can also be rejected if incident and transmitted intensity measurements are made simultaneously. The approximate dependence of the minimum detectable absorbance on the full well capacity of a detector element is given by:

$$A_{min} \approx - \log (1 - (8/Q_{sat})^{1/2}) \qquad (4)$$

where Q_{sat} is the saturation level of the detector element and represents the signal charge measured with no absorbing species present in the sample beam. As an example, a CTD with a full well capacity of 1 million charge carriers is capable, by this model, of detecting an

absorbance as low as 1.2×10^{-3} absorbance units. A CTD with a saturation level of 10 million charge carriers should be able to detect an absorbance of 3.9×10^{-4} A.

Detectors with significantly higher noise levels than optimized CCD's are acceptable for absorption measurements as opposed to luminescence measurements since photon shot noise and/or fluctuation noise dominate. Some shot noise from the dark current can also be tolerated making it possible to operate the detector at a warmer temperature. For these reasons, thermoelectrically cooled linear scientific PDA's make acceptable detectors for molecular absorption applications in spite of their comparatively high read noise.

Sensitivity in High Background Situations

In many cases, particularly when complex samples are being analyzed, the ultimate sensitivity attainable in an emission experiment (flame and plasma atomic spectroscopy) is dictated not by the ability of the detector to measure a small flux, but by the ability to detect a small signal superimposed on an intense background. In this case, or in any spectroscopic measurement where a significant background is present, CTD and PDA detector element saturation level often determines the minimum detectable signal. This occurs in a way analogous to the way detector element saturation level determines the minimum absorbance detectable with an integrating photodetector.

In the emission measurement, the subtraction of the background signal from the analyte plus background signal must result in a value

statistically greater than zero for the analyte to be detected. The calculation of the minimum detectable flux superimposed on a background is performed in a manner similar to the minimum detectable absorbance calculation. As might be expected, a similar result is obtained. The ratio of the minimum detectable flux in terms of charge carriers generated during the total exposure time to the detector element saturation level is given by:

$$I_{min}/Q_{sat} = (8/Q_{sat})^{1/2} \qquad (5)$$

Detection limits which are limited by background emission may be improved by increasing detector full well capacity until the point where integration time becomes so long that source drift becomes the limiting factor. This result is similar to the one obtained for absorption measurements. The two results (equations 6 and 7) are plotted in Fig. 1. An example calculation for the case of a CTD with a saturation level of 1 million and 10 million charge carriers gives minimum detectable differences of 2828 and 8944 charge carriers respectively. In terms of a fraction of the device full well capacity (fraction of the background intensity) the results are 0.28 % and 0.09 %.

Using this model, spectrometer throughput and detector quantum efficiency are not critical. In real analytical systems however, higher throughput and better QE minimize the effects of source fluctuation by reducing measurement time. Lower background analytical sources are the real key to improved sensitivity in background shot noise limited measurements.

Spectrometers for use with Silicon CTDs and PDAs

Effective use of CTDs and PDAs in analytical spectroscopy requires the use of different optical configurations than those found in systems employing PMTs or photographic film. This section provides an overview of some of the experimental configurations devised to efficiently use linear and two-dimensional solid-state arrays. The examples were chosen both to illustrate the flexibility of detection with an array of contiguous detectors, and to demonstrate the very high performance obtainable with modern CTD's.

One Dimensional Dispersive Spectrographs

Conventional spectrographs disperse light across a curved focal plane of 100 to over 1000 mm in length. When using a linear CTD or PDA for spectroscopic measurements which do not require very high resolution, it is necessary to disperse light from 200 to 900 nm across a flat detector which is only 10 to 50 mm wide. The use of flat-field concave holographic gratings designed specifically for solid-state array detectors provides a simple single element spectrograph with low dispersion and very high throughput.

Linear scientific PDAs have relatively wide (25 μm) detector elements with 100 to 1 height to width aspect ratios (2.5 mm tall).[15] This makes these devices relatively compatible with spectrometers which employ tall narrow slits. Most linear CTDs have small, nearly square, detector elements typically only 5 to 15 μm on a side. Efficient use of these detectors requires some form of image size reduction.

This reduction can be achieved in a number of ways including using an entrance aperture which matches the height to width aspect ratio of the detector elements and either imaging a small aperture directly or using a short focal length camera optic as compared to the focal length of the collimating optic (magnification less than 1). Alternatively, the image of a tall slit can be compressed with a cylindrical lens.

Spectrographs can be constructed which have moderate resolution and good sensitivity over the ultraviolet and visible wavelength range using a linear CCD. A device having 3456 detector elements such as the Texas Instruments virtual phase TC104[16] can be employed to cover the wavelength range of 200 to 900 nm at approximately 2 nm per detector element. *The very high quantum efficiency and low read noise of linear virtual phase CCD's makes possible the design of a spectrometer system which is predominantly limited by shot noise from stray and scattered light.*

One dimensional dispersive spectroscopy with a two dimensional CCD detector allows the custom matching of detector element to slit image size through a process called binning. Binning is the combining of charge from more than one detector element. Detector elements located along a common column may all be illuminated by a tall vertical slit. Binning the photogenerated charge from all of these detector elements results in a signal proportional to the sum of all of the charge but with the read noise of a single detector element. Binning of charge and subjecting a charge packet to only one read can result in greatly increased SNR compared to reading out every detector element

individually and summing the signal levels in computer memory. SNR can be further improved at the expense of resolution by binning in the direction of dispersion. Binning factors can even be varied dynamically so that sensitivity can be improved in one region of a spectrum while high resolution is maintained in another.

Two Dimensional Dispersive Spectrographs

The two dimensional format of many CCDs and CIDs can be efficiently used for high resolution spectroscopy when coupled with an echelle spectrometer. The same considerations discussed above for producing image sizes compatible with the format of the detectors for spectrometers dispersing the light in one direction apply for echelle spectrometers. The optical block diagram of such an echelle spectrometer developed in these laboratories for use with CTDs is shown in Fig. 2.

The echelle spectrometer is currently being employed with a CID for plasma emission spectroscopy. An example of an emission spectrum observed with the system is shown in Fig. 3. The CID has 92,232 active detector elements and the spectrometer covers the wavelength range from 225 nm to 515 nm at 0.02 to 0.04 nm per detector element. The spectrometer used for this work is similar in principle to echelle spectrometers designed for use with photographic film; however, seven fold image size reduction is used in order to produce an echellogram compatible in size with the detector.

The CID's ability to handle very wide dynamic range signals is the key to the success of this instrument. The system monitors the photon flux at very faint spectral features located amidst very intense ones by using random access integration (RAI) detection. The very specialized read mode of the CID described in the first article of this series, called the non-destructive read out (NDRO), enables charge accumulation to be monitored during the course of an exposure and integration times to be varied dynamically based on the signal level at every spectral line.[17] The photogenerated charge information accumulated in a detector element is left undisturbed by the NDRO so the charge storage process can be monitored as it is occurring. Trace level components can be determined at the same time as components present at the percent level in a single exposure.

The flexibility afforded by the system in terms of wavelength selection is a second important feature. The choice of spectral lines to be used for an analysis can be custom tailored to the components of the sample at hand. The most intense spectral lines of an element can be selected for components present at very low levels and less intense lines resulting from non-resonance transitions are used for elements at high concentrations in order to avoid problems with self absorption. Multiple spectral lines are used for each element to enhance precision and known spectral interferences are avoided in the cases where other spectral lines are available. Background correction procedures are applied to every spectral line using the data from adjacent detector elements.

The number of detector elements employed in the present CID/echelle spectrometer system is rather low compared to what is available with modern CCD detectors. The use of a large CCD with an echelle spectrometer would allow the attainment of much higher resolution at the same or increased wavelength coverage. Calculations show that large CCDs coupled with an echelle spectrometer should be capable of achieving the approximately 0.001 nm resolution over the ultraviolet and visible wavelength range that is necessary for continuum source atomic absorption spectroscopy. Besides offering simultaneous multielement capabilities as in emission spectroscopy with a CID, the flexibility of choosing spectral lines is available. The micro-sampling furnace techniques that are available for use in atomic absorption spectroscopy combined with a simultaneous multielement spectrometer would make a very powerful analytical tool for trace element analysis when sample size is limited.

One Dimensional Dispersive Spectroscopy Providing Temporal Information

Several interesting applications of two dimensional CTDs use only one axis for the dispersion of light. One example is the use of a CCD for rapid scanning UV-visible spectroscopy.[18] In this application, the output of a polychromator is imaged onto only one row of detector elements in a two dimensional CCD. No light is allowed to fall on any of the other detector elements. The remaining rows of the imager are used to store, in analog form, the spectral information recorded in the

illuminated row. Figure 4 shows schematically the arrangement used for fast spectral framing.

The spectral information from an integration period is stored simply by rapidly shifting the photogenerated charge from the last row into the next row as illustrated in figure 4. The time required to shift a row can be as fast as 2 μsecs, thus spectra can be recorded at a rate up to 500 KHz. The maximum number of spectra that can be collected is dictated by the number of rows in the CCD, typically ranging from several hundred to over two thousand. Also, since the delay between shifts is under direct computer control, the rate of acquiring spectra can vary from a maximum of 500 KHz to as slow as necessary. For example, if an exponentially decaying luminescence event is being observed, the time between shifts can be successively lengthened to better follow the decay. This has the advantage of recording data frequently when the signal intensity is high and changing rapidly, and allowing longer integration times when the signal is at its weakest.

This rapid scanning spectrometer approach has several advantages over conventional rotating mirror single channel rapid scanning spectrometers. Recording the intensity at all wavelength intervals simultaneously has the advantage of greater sensitivity. The improvement, given equal sensitivity detectors, is in proportion to the square root of the number of wavelength intervals (detector elements). Since the CCD is actually a more sensitive detector than a PMT, the improvement is greater than this. Mechanical problems associated with moving a mirror at constant velocity are avoided. Additionally, the maximum

spectral acquisition rate is 100 to 1000 fold greater with a CCD than with mechanical systems. Figure 5 shows a time resolved spectra of a Xenon flash lamp recorded with a 320 by 512 element CCD.

Spectroscopic Imaging

A variety of other spectroscopic problems have been solved employing the imaging capabilities of CTDs. One example is the measurement of the absorbance of very opaque thin films.[19] Research into the parameters affecting crystal formation in the vapor deposition of thin vanadium-phthalocyanine films used in solar energy conversion studies resulted in the creation of optically opaque films which contained small pinholes. The absorbance of the films varied from 1.5 to 5 absorbance units over the wavelength range 550 to 860 nm. The presence of the pinholes, which were essentially transparent, prevented accurate absorption measurements from being made in a conventional absorption spectrometer. Additionally, even in the absence of pinholes, stray light in a conventional spectrometer limits the maximum absorbance measurable to 3 absorbance units.

Accurate absorbance measurements were obtained for these films by placing the films at the exit slit of a double monochromator and imaging the transmitted light onto a CCD array detector. The double monochromator increases the stray light rejection characteristics of the instrument. The CCD allows the spatial discrimination against pinholes and the selection of only uniform, pinhole-free areas of the phthalocyanine films for the measurement of transmitted intensity. Even

with the reduced throughput of the double monochromator, the CCD was able to measure absorbance values in excess of 5 absorbance units. Figure 6 shows the image of one of these phthalocyanine films.

Another example of a low light level imaging problem that is currently being solved by the use of a CCD detector in fluorescence microscopy.[20] Fluorescence microscopy has a number of advantages over conventional microscopy including: a cell component or probe can be detected in the presence of a large excess of other species; fluorescent probes can be tailored to measure physical properties such as pH, ion concentrations and enzymatic activity in intracelluar compartments; and quantitation at extremely low concentration levels is possible due to the inherent sensitivity of fluorescent techniques.

The ultra high sensitivity and high geometric accuracy of CCDs are important in the technique of optical sectioning which allows the reconstruction of three-dimensional images of cell organelles from two-dimensional fluorescence images.[21,22] Fig. 7 is a digital image of a bacteriophage DNA molecule which has a fluorescent tag adsorbed onto the major groove of the DNA molecule.[23] The tag fluoresces only when bound to DNA and does not fluoresce when either unbound or when bound to RNA. This single image is one of a group used in three-dimensional image reconstruction. The use of a CCD is crucial to this technique as intensified silicon intensified target vidicons (ISITs) do not provide the geometric stability, the dynamic range, the linearity nor the sensitivity necessary to perform a high quality image reconstruction.

Conclusion

Significant SNR benefits are possible when high quality multi-channel detectors such as CIDs and CCDs are employed in place of single detectors such as PMTs in analytical UV-visible spectroscopy. In addition to the multichannel advantage, CTDs have sufficiently high sensitivity and dynamic range to provide comparable or superior performance in luminescence, absorption and emission spectroscopy when considered on a single detector element basis. These properties, as well as the availability of CIDs and CCDs in a large number of sizes and formats, make the application of multichannel detection to spectrochemical analysis practical. Polychromators which allow complete flexibility in wavelength selection are already in use as are a new generation of higher sensitivity and higher speed rapid scanning spectrophotometers. The adaptation of CTD detector technology to other areas of analytical spectroscopy is currently underway, with solid-state detectors rapidly replacing vacuum tube detectors in many applications.

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TABLE 1

SNR comparison of multichannel and multiplexed methods

versus single channel methods

Type of dominant noise source	$SNR_{MC,pmt}/SNR_{SC,pmt}$[a]	$SNR_{MC,ctd}/SNR_{SC,ctd}$	$SNR_{MX,pmt}/SNR_{SC,pmt}$
noise = constant[b] (detector noise)	$N^{1/2}$	N	$N^{1/2}$
noise $\propto$ (signal)$^{1/2}$ (photon shot noise)	$N^{1/2}$	$N^{1/2}$	1[c]
noise $\propto$ signal (fluctuation noise)	1[d]	1	$1/N^{1/2}$[e]

[a] MC = multichannel, SC = single channel, MX = multiplexed, N = the number of channels.

[b] Detector noise in photomultiplier tubes and photoconductors results from shot noise in the dark current. The noise has a square root dependence on time. Detector noise in CTDs and PDAs is associated with the read process and is independent of time, thus the different results when detector noise is dominant.

[c] These results are obtained when signal as a function of wavelength is constant. If there i structure in the spectrum, photon-shot-noise tends to degrade the SNR in the vicinity of intense spectral features. Fluctuation noise also tends to be localized in the vicinity of strong spectral features. In the extreme case of line spectra, evaluation of the SNR figure of merit when fluctuation or photon shot noise is dominant is not possible because it varies from line to line and depends on the complexity of the spectrum.

[1]In some cases, a multichannel advantage may exist in fluctuation noise limited systems. For the same SNR, measurement time is reduced by a factor of N. This shifts the measurement bandwidth to higher frequencies. Fluctuation noise may be less significant at higher frequencies because of its approximate proportionality to $1/f$.

[a]Assumes approximately uniform intensity throughout spectrum.

TABLE 11

Characteristics of Optimized CID, CCD, PDA and Photon Counting PMT Systems

System	Respossivity Range	Peak QE	# elements	Element size	Dark Current (e⁻/second)	Read Noise (e⁻)
CCD(TI 800 x 800 3 phase backside)[a]	.1 to 1000 nm	90%	640,000	15 x 15 m	0.001 (173K)	5
CID(GE CID17 244 x 377)[b]	200 to 1,000 nm	50%	94,672	24 x 27 m	0.008 (135K)	60 (w/NDRO)
PDA (Reticon 1024S)[c]	200 to 1,000 nm	73%	1,024	25 m x 2.5 m	624 (193K)	1200
PMT (Galileo Electro-Optics)[d]	200 to 650 nm	18%	1	0.3 x 3.0 mm	3 (253K)	N.A.

[a] J. Janesick, D. Campbell, T. Elliott, T. Daud, P. Ottley "Flash technology for CCD imaging in the UV" in UV Technology, R. Huffman Ed., Proc. SPIE 687, 36 (1986).

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[c] reference 1, 15

[d] reference 13

[e] averaging of nondestructive read outs to reduce noise

Figure Captions

Fig. 1. a. Minimum detectable absorbance (MDA) plotted as a function of detector element saturation level for an integrating detector. See equation 6.

b. Minimum detectable flux as a fraction of device saturation level plotted as a function of saturation level for an integrating detector. This curve represents the minimum flux that is detectable in a high background situation. See equation 7.

Fig. 2. Optical block diagram of an echelle spectrometer designed for use with a CTD detector. A focal plane image covering the wavelength range of 225 to 515 nm is created in an area 6.5 mm tall by 8.7 mm wide by employing a 75 cm focal length collimating parabola and a 10 cm focal length camera optic.

Fig. 3. Background subtracted echelle emission spectrum of Iron produced in a direct current argon plasma and recorded with a CID camera.

Fig. 4. Block diagram of the operation of a CCD in fast spectral framing mode. A linear spectrum is dispersed across one row of the sensor and the image stored in analog form by rapidly shifting the photogenerated charge under an opaque mask. Acquisition times as short as 2 μsecs are possible and up to 2000 spectra may be recorded.

Fig. 5. Xenon flash lamp time resolved emission spectrum recorded with a CCD camera. Spectra were recorded at 6 μsec intervals and every fourth spectrum was plotted.

Fig. 6. CCD image of an opaque phthalocyanine film illuminated with 650 nm light from a double monochromator. Absorbance at this wavelength of the pinhole free regions is 3.4 absorbance units. The outlined region was used for the measurement of transmittance for the sample and blank. This region was adjusted to pinhole free areas for each film.

Fig. 7. Image of a fluorescently tagged bacteriophage DNA. The tag binds to the major groove and only fluoresces in this form. The fluorescence is excited at 365 nm (Hg, 12 nm FWHM) and observed at 480 nm using a 395 nm dichroic barrier filter and a 410-560 nm bandpass filter. A highlight level of 30,000 electrons resulted form a 30 second exposure of the 640X1024 element CCD. The photograph is a 170 nm spatial resolution image of a 2 nm diameter DNA strand. Photo courtesy of Y. Hiraoka, D.A. Agard and J.W. Sedat.

APPENDIX 1

Signal-to-noise ratio equations used for the comparison of
spectroscopic methods. Equations 1, 3 and 5 are adapted from reference
3 and consider detectors such as PMTs and photoconductors. Equations 2
and 4 apply to integrating detectors such as CTDs and PDAs.

$$SNR_{sc,pmt} = \frac{t/N(R_1)}{[t/N(R_d + R_b + R_1) + t^2/N^2(\xi^2 R_1^2 + \xi_b^2 R_b^2)]^{1/2}} \qquad (1)$$

$$SNR_{sc,ctd} = \frac{t/N(R_1)}{[N_r^2 + t/N(R_b + R_1) + t^2/N^2(\xi^2 R_1^2 + \xi_b^2 R_b^2)]^{1/2}} \qquad (2)$$

$$SNR_{mc,pmt} = \frac{t R_1}{[t(R_d + R_b + R_1) + t^2(\xi^2 R_1^2 + \xi_b^2 R_b^2)]^{1/2}} \qquad (3)$$

$$SNR_{mc,ctd} = \frac{t R_1}{[N_r^2 + t(R_b + R_1) + t^2(\xi^2 R_1^2 + \xi_b^2 R_b^2)]^{1/2}} \qquad (4)$$

$$SNR_{mx,pmt} =$$

$$\frac{(1/2)R_1}{[tR_d + t/2(\sum_{i=1}^{m} R_{1i} + \sum_{i=1}^{m} R_{bi}) + t^2/4(\sum_{i=1}^{m} \xi_{1i}^2 R_{1i}^2 + \sum_{i=1}^{m} \xi_{bi}^2 R_{bi}^2)]^{1/2}} \qquad (5)$$

where:

t	= total measurement time
N	= number of channels used (features measured)
R_1	= count rate due to analyte
N_r	= detector read noise
R_d	= dark current rate
R_b	= count rate due to background
ξ_1	= flicker constant for analyte signal
ξ_b	= flicker constant for background signal

The type of detector noise that must be considered depends on the type of detector being employed. In the infrared region of the spectrum, the state-of-the-art detectors are photoconductive detectors such as the MCT (mercury-cadmium-telluride) detector. When properly cooled and shielded from background infrared radiation, the detector is capable of performing at the Johnson noise limit. If the detector is not sufficiently shielded then the detector performs as a background limited infrared photodetector (BLIP). In either case, the noise has a square root dependence on time (bandwidth).

Photomultiplier tubes operating in the ultraviolet-visible region of the spectrum are also limited by a time dependent noise source. In this case it is shot noise from the dark current. The noise is given by the square root of the product of the dark current rate and the integration time.

Calculation of the ratios of SNR performance achievable with systems employing these types of detectors result in the following:

$$\frac{SNR_{mc}}{\overline{SNR}_{sc}} = (N)^{1/2} \qquad (6)$$

$$\frac{SNR_{mx}}{\overline{SNR}_{sc}} = 1/2(N)^{1/2} \qquad (7)$$

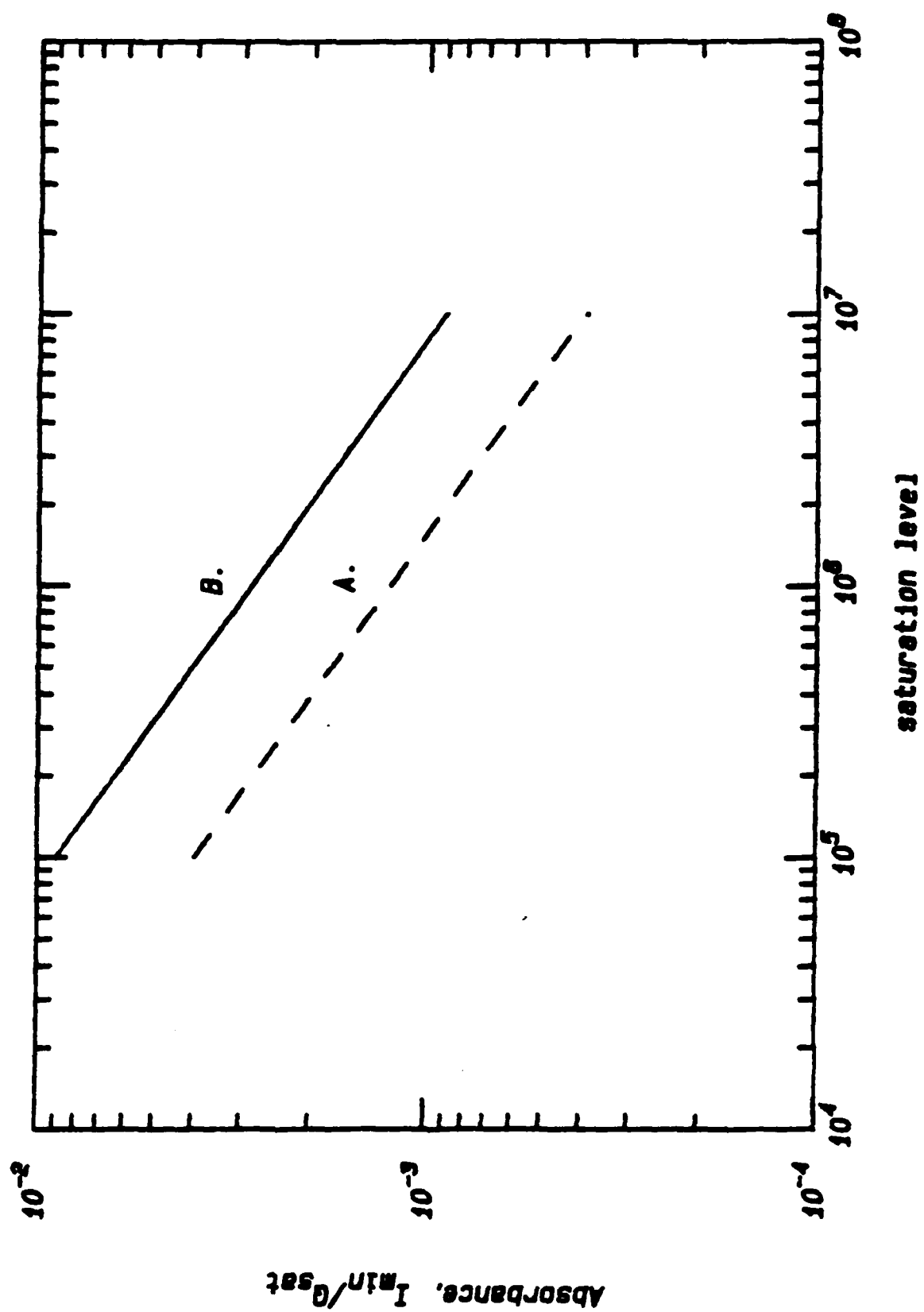These results are shown in line 2 of table 1.

Integrating detectors such as the silicon CTDs and PDAs can be cooled sufficiently to virtually eliminate dark current and its associated noise. However, these detectors have a time independent read noise. This noise is unchanged regardless of the integration time employed prior to read out. The multichannel versus single channel advantage for this type of detector is,

$$\frac{SNR_{mc}}{\overline{SNR}_{sc}} = N \qquad (8)$$

These results illustrate several interesting points. The multichannel advantage achieved when employing integrating detectors is greater than the one achieved when using current detectors. This is because of the linear improvement in SNR with time that is possible with these detectors.

The use of an integrating detector in a Michelson Interferometer is not considered because the recording of a signal that is rapidly changing in time with an integrating detector is not desirable. Detector read noise is introduced with every sampling of the time varying signal. If an integrating detector must be employed with a

Michelson interferometer, the best SNR can be achieved with a single scan of the mirror and with as few samples as possible. A much more effective way to record an interferogram with an integrating detector is to record the interferogram spatially rather than temporally. Rather than using a Michelson interferometer, effective use of an integrating multichannel detector can be made with a holographic interferometer (a tilted mirror Michelson interferometer). In this type of system, the advantages of high light throughput and absolute wavelength accuracy are combined with many of the desireable features of multichannel detectors.
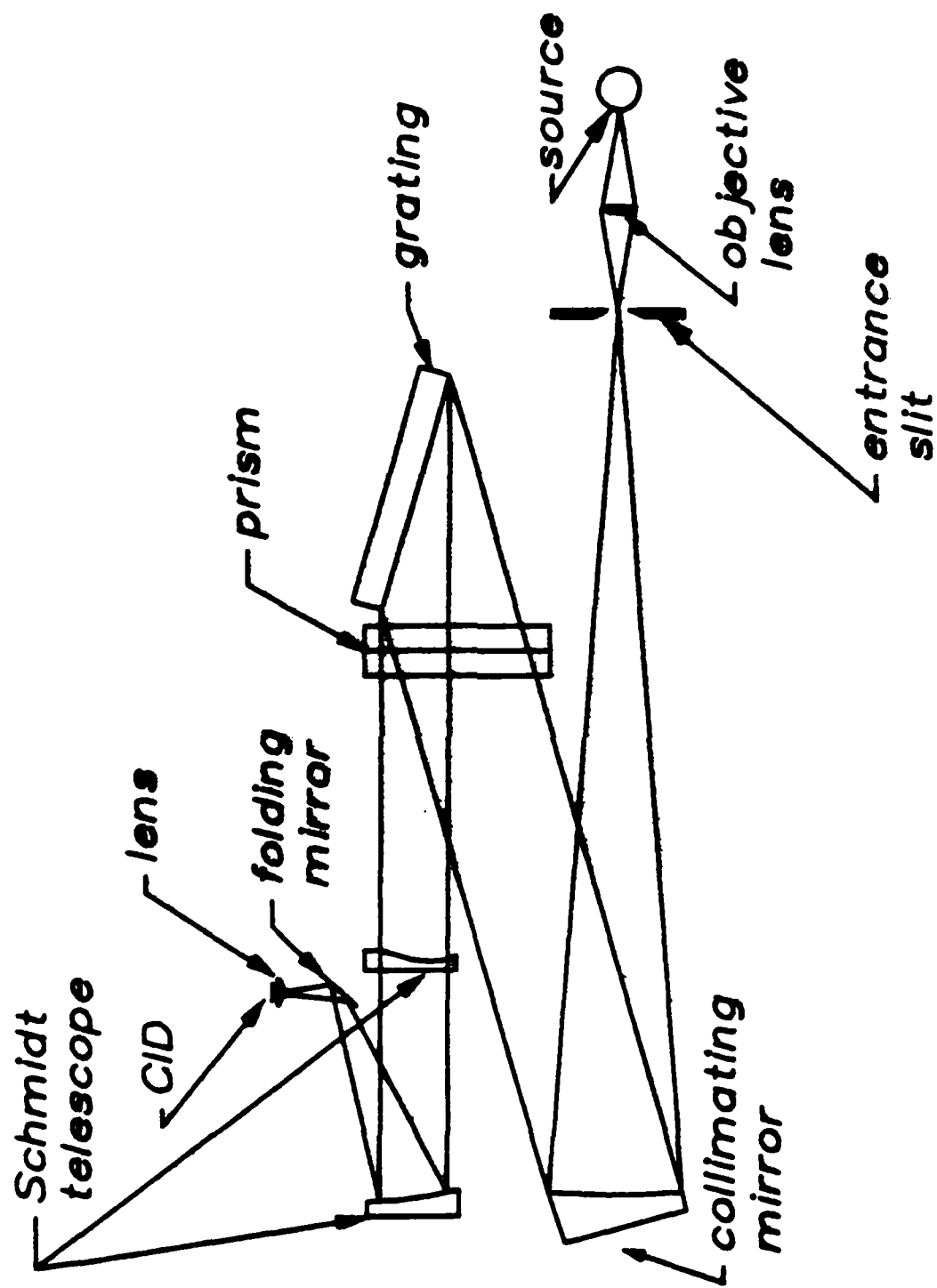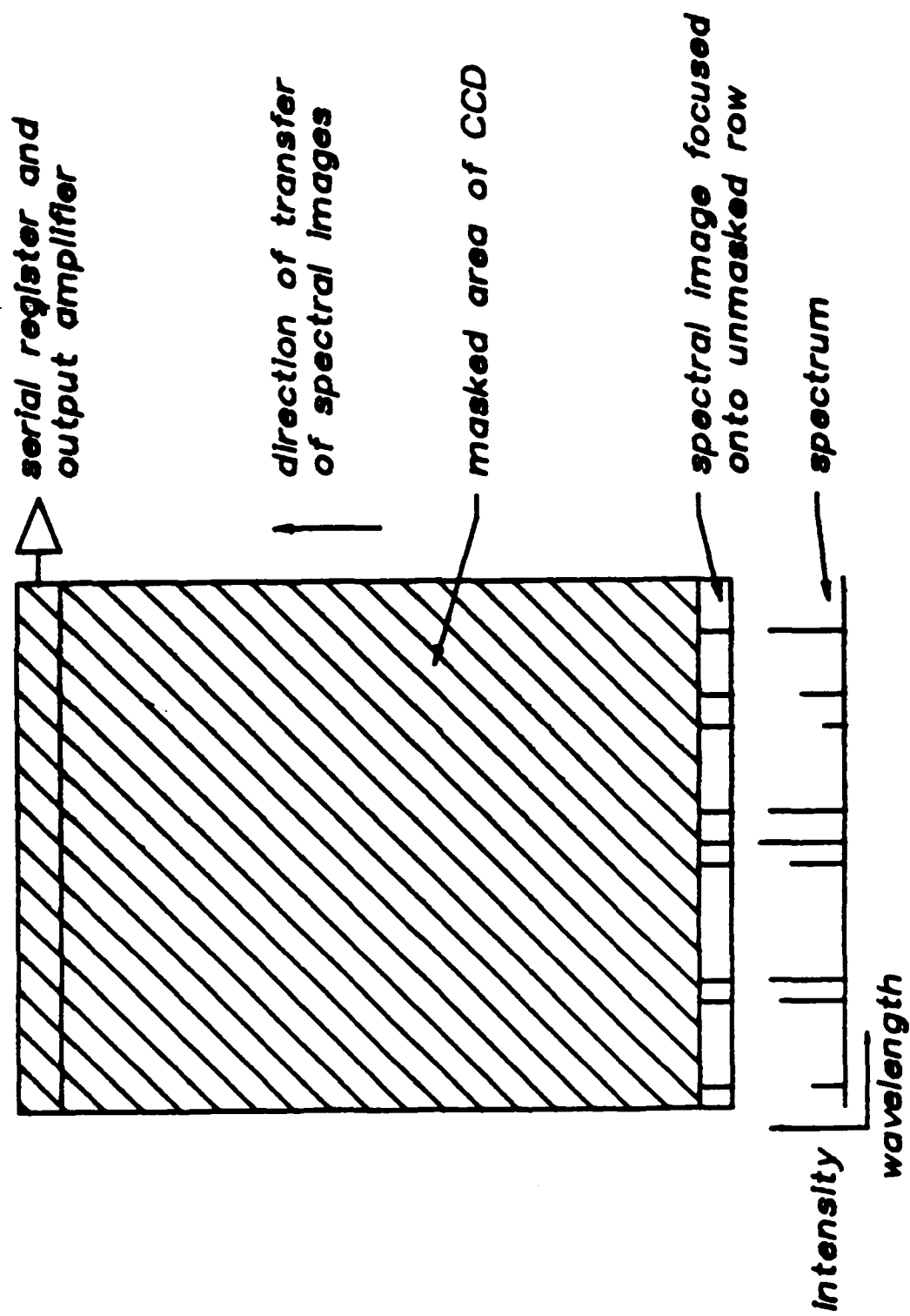
Absorbance, I_{min}/Q_{sat}

saturation level

Figure 1

Figure 2

Figure 3

serial register and
output amplifier

direction of transfer
of spectral images

masked area of CCD

spectral image focused
onto unmasked row

spectrum

Intensity

wavelength

Figure 4

TIME RESOLVED SPECTRA OF A XENON FLASH

INTENSITY

1200
1000
800
600
400
200

TIME (μ secs)

100
500
800
700
900

WAVELENGTH (nm)

700   704   708   712   716   720   724   728
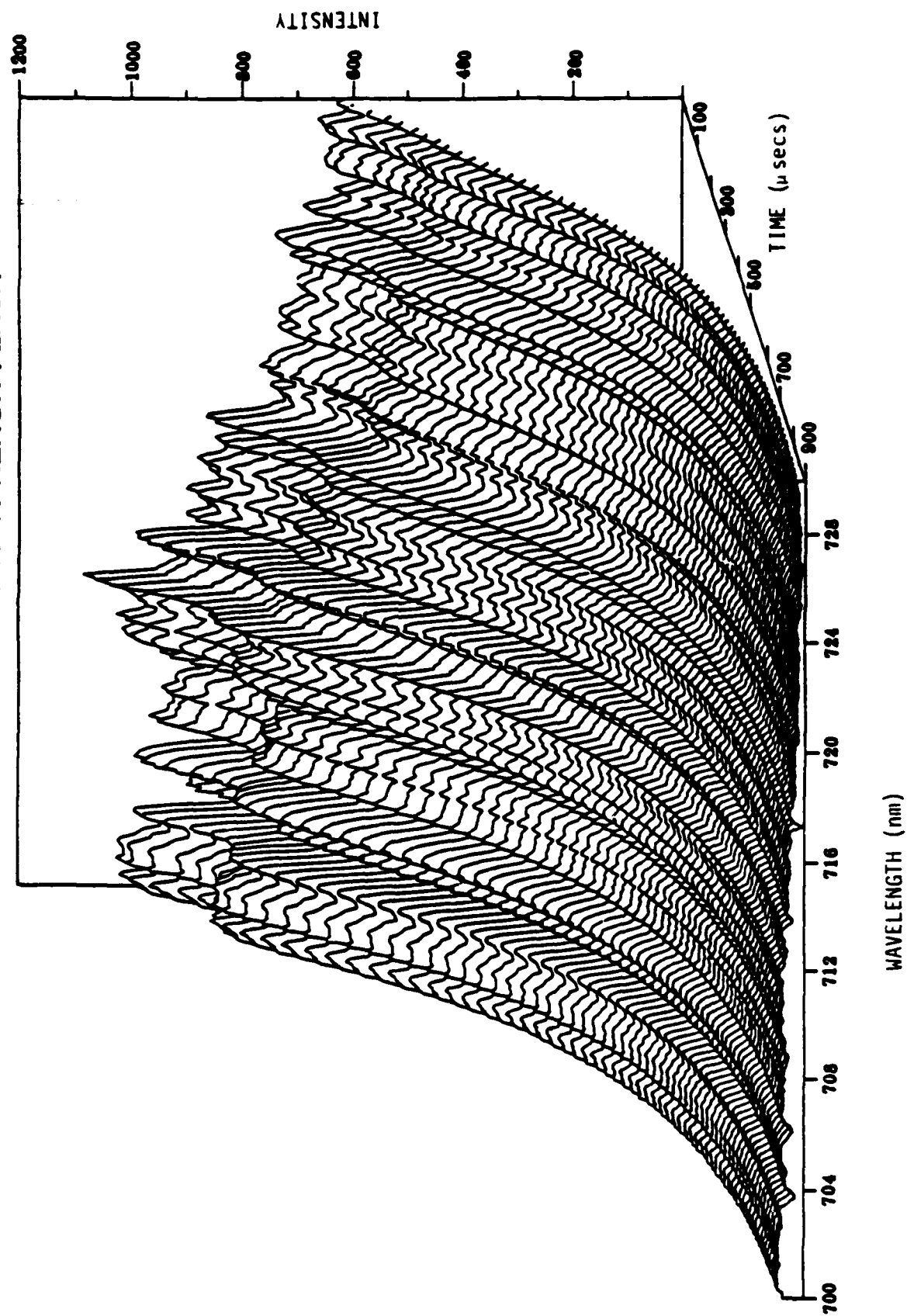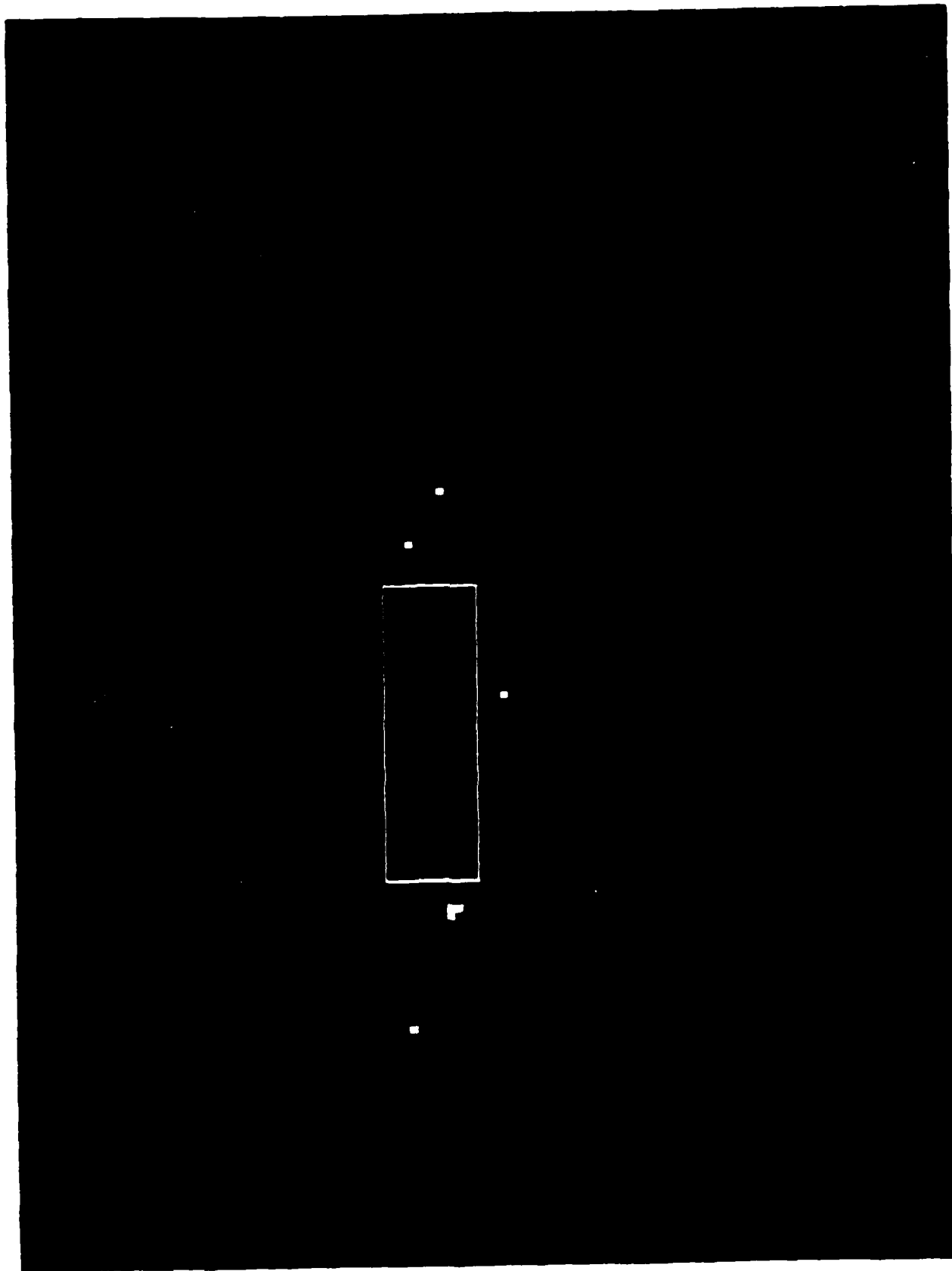
Figure 5

Figure 6

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